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Heteropoly compounds are excellent catalysts for both acid and oxidation chemistries. In our research we have used phosphomolybdic acid, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, (PMo) as a possible oxidation catalyst. However, the activity of PMo can be increased by the incorporation of vanadium and copper to give $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ (PMoV) and $\text{H}_6\text{PMo}_{10}\text{CuVO}_{39}$ (PMoCuV). As part of a larger study to fully characterize the structure and activity of the novel $\text{H}_6\text{PMo}_{10}\text{CuVO}_{39}$ catalyst, we have used x-ray absorption spectroscopy (EXAFS and XANES) to investigate the local structure around copper as well as to determine the oxidation states of the incorporated transition metals (Cu, V and Mo).

These types of heteropoly compounds assemble into well-defined local structures called Keggin units. The Keggin unit is composed of a PO_4 tetrahedron surrounded by twelve transition metal octahedra. In our sample, molybdenum is located in the octahedra. Other transition metal atoms can be substituted in place of molybdenum with only a slight distortion of the structure.

X-ray absorption studies were first performed at the molybdenum K edge on the PMo, PMoCuV, and MoO_3 . As is shown in Figure 1, the PMoCuV sample showed a radial structure function similar to a commercial PMo sample, indicating Keggin units were present in the synthetic PMoCuV sample. The peak at 3.1 Å is due to presence of molybdenum in the second shell. Analysis of the near edge data indicated the molybdenum is in a +6 oxidation state as expected.

Once the presence of Keggin units had been verified, the local structure around the copper was determined. As shown in Figure 2, the major peaks in the copper radial structure function have been assigned to copper-oxygen distances only. From these data, the copper apparently did not substitute isomorphically for molybdenum in the Keggin structure under our synthesis conditions. Edge data are consistent with copper existing in the +2 oxidation state in the heteropolyacid sample.

Finally XANES analysis at the vanadium K edge showed the vanadium was in a +5 oxidation state in both the PMoV and the PMoCuV samples.

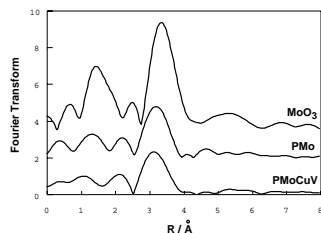


Figure 1. Radial structure function at the Mo K edge for various samples.

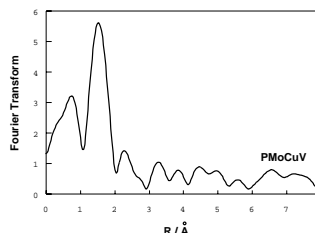


Figure 2. Radial structure function of PMoCuV at the Cu K edge.